USGS

WATER RESOURCES RESEARCH GRANT PROPOSAL

Title: A novel *in situ* technology for the treatment of groundwater contaminated with agriculturally-derived nitrate

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Statement of Critical Regional or State Water Problems

Heavy fertilizer use has been identified as the principal source of nitrate that is found in shallow rural aquifers. Agriculturally-derived nitrate contamination of groundwater is a significant problem on the local, regional, and national levels. A 1990 survey of wells conducted by the USEPA suggests that 5 % of all U.S. wells contain nitrate that exceeded the maximum contaminant level (MCL) of 10 mg/l of nitrate. This suggests that 4.5 million people in the U.S. are exposed to high levels of nitrate through their water supply (Nolan *et al*., 1998). According to the USGS, the areas of highest risk for groundwater contamination by nitrate include large portions of the Midwest, as well as parts of the western and northeastern United States (Nolan *et al*., 1998). In Minnesota, data collected between 1992 and 1996 indicate that 14 % of the state's groundwater supplies have nitrate levels greater than 1 mg/l, and 4 % of sites have levels exceeding the standard of 10 mg/l (Minnesota Pollution Control Agency, 1998).

Increasing nitrate levels across the U.S. represent increasing risks to public health and environmental quality. High concentrations of nitrate in drinking water particularly threaten infants younger than six months old. Methemoglobinemia (blue baby syndrome)

in infants can result when formula is mixed with water containing nitrate. Blue baby syndrome impairs an infant's ability to maintain sufficient blood oxygen levels and can cause death in those affected. Research has also suggested that nitrate may play a role in the development of some cancers (United States Department of Heath, 1999).

Current treatment options for the removal of nitrate from contaminated drinking water supplies are expensive or create additional water quality problems. Ion exchange, a physical-chemical process to remove ions from water, is fairly effective for the treatment of nitrate-contaminated water. However, this process produces large quantities of brine that must be subsequently disposed of (Gauntlett, 1981; Hollò and Czakò, 1987). When used for the removal of nitrate from significant volumes of water, the process is not cost effective. Biological denitrification is also an effective treatment process for the removal of nitrate from contaminated water. However, biological denitrification requires the addition of an electron donor (often an organic substrate), which may impact water quality by increasing residual biochemical oxygen demand in the effluent. Biological denitrification can also result in the production of undesirable levels of biomass in the effluent.

The use of autotrophic denitrification can overcome some of these concerns. In particular, the use of hydrogen gas (H_2) for denitrification can selectively remove nitrate (Rutten and Schnoor, 1992). In addition, the low concentrations of H_2 added to the water can be readily removed by aeration and pose no health concern (Gros *et al.*, 1988) and less biomass is produced in autotrophic systems. Biological denitrification also may be conducted in the aquifer (*in-situ*) (Mercado *et al*., 1988; Hiscock *et al*., 1991), in which the aquifer is employed as a reactor for the reduction of nitrate from groundwater. The major advantage of this process is that the aquifer can be served as both a biochemical reactor and filter, therefore resulting in water that requires no special treatment beyond that already employed by the existing water utility. One problem that remains with in situ autotrophic denitrification is the issue of H_2 addition to the aquifer.

Statement of Expected Result or Benefits

The proposed research will work to alleviate the health threats of nitrate contamination of groundwater. Biological denitrification *in situ* represents a comparatively inexpensive and effective mechanism for nitrate removal. Autotrophic *in situ* denitrification produces no byproducts and makes use of the natural filtration of the aquifer thereby avoiding costs associated with the removal of toxic organic compounds and excess biomass. The use of hollow fiber membranes for H_2 addition to the aquifer will provide a safe and effective (100% efficient gas transfer) means to supply H_2 to the subsurface.

Nature and Objectives of the Research

While several laboratory studies have confirmed that this process is a viable mechanism for denitrification, little is known about the implementation of such a system into a field situation. Therefore, the overall objective of this research is to determine the viability of *in situ* autotrophic denitrification using membrane-delivered H_2 for the remediation of

nitrate-contaminated drinking water supplies. To reach the overall goal, four incremental objectives are proposed.

1. Assess the long term performance of hollow fiber membranes in terms of their ability to deliver H_2

2. Determine *in-situ* denitrification kinetics and model the autotrophic removal of nitrate in an aquifer

3. Determine the stoichiometric requirements for H_2 delivery as a function of groundwater quality

4. Document any changes in total organic carbon and biological quality caused by the use of H_2 in the subsurface

Background

Biological denitrification is a natural process through which bacteria use reduced nitrogen (NO_3^- or NO_2^-) as a terminal electron acceptor, forming N_2 (Nicolson, 1979; Winkler, 1981; Bouwer and Crowe, 1988). Electron donors are required for this process to proceed and can consist of organic compounds such as methanol or acetic acid, reduced sulfur compounds, or H_2 (Winkler, 1981; Batchelor and Lawrence, 1978; Hiscock *et al*., 1991).

As a treatment option for the removal of nitrate from drinking water, biological denitrification represents a more cost-effective and versatile approach than ion exchange, particularly as the plant size increases (Gauntlett, 1981). Biological denitrification is not only able to remove nitrate but it is also able to eliminate various toxic micropollutants and organic mutagens (Rogalla *et al*., 1990; Kool and Van Kreijl, 1984; Bouwer and Crowe, 1988, and Larzarova *et al*., 1992). Biological denitrification also can be conducted *in situ* whereas ion exchange is limited to application as surface water treatment process at a water treatment plant.

Much work has been conducted in Europe on the use of biological denitrification for drinking water treatment. Heterotrophic denitrification has been has been marketed in France, Germany, and the Netherlands for drinking water denitrification since the 1980s (Rogalla *et al*., 1990; Richard, 1989; Boehler and HaldenWang, 1992; van der Hoek and Klapwijk, 1987). However, in the United States the use of biological denitrification has been limited by a variety of concerns (van der Hoek and Klapwijk, 1987; Sorg, 1980). In the case of heterotrophic denitrification, there are significant health concerns associated with adding organic carbon sources such as methanol to drinking water for the bacteria respiration and growth because incomplete removal of organic compounds in the denitrified water may lead to bacterial regrowth in water distribution systems. Furthermore, the deliberate cultivation of microorganisms increases the risk of bacterial

contamination in the product water. Because of this, subsequent treatment and disinfection processes are required to remove the introduced bacteria and organic residuals (Hijnen *et al*., 1988).

The use of autotrophic denitrification can overcome some of these concerns, as mentioned above. In recent years, autotrophic denitrification with H_2 has been applied for the reduction of nitrate from drinking water supplies in lab-scale and full-scale treatment. These studies have shown that the process is technically and economically feasible for nitrate removal from drinking water supplies (Dries *et al*., 1988; Rutten and Schnoor, 1992; Clifford and Liu, 1993). In addition, biological denitrification offers the flexibility of application in the drinking water aquifer itself or as a conventional above ground treatment process (Mercado *et al*., 1988; Hiscock *et al*., 1991). As mentioned above, *in-situ* denitrification employs the aquifer as a reactor for the reduction of nitrate from groundwater. The major advantage of this process is that the aquifer can be served as both a reactor and filter. Consequently, water pumped from the ground down-gradient of the H_2 injection point may require no special treatment. In addition, *in-situ* denitrification is not influenced by seasonal temperature variations (Hiscock *et al*., 1991) and this type of installation can save considerable capital and operating costs (Dahab, 1991).

All of the *in situ* denitrification studies to date have focused on the injection of organic compounds to foster heterotrophic denitrification (Janda *et al*., 1988; Kruithof *et al*., 1988; Mercado *et al*., 1988). The use of H_2 injection to the subsurface for autotrophic denitrification has not been studied because H_2 is sparingly soluble, flammable, and when conventional gas transfer devices are used, much of the gas is vented and lost to the atmosphere. This inefficiency in H_2 gas transfer can increase the cost of electron donor addition and gives rise to safety concerns. However, new membrane technologies for gas transfer are capable of H_2 dissolution with 100% efficiency (Ahmed and Semmens, 1992; Semmens and Ganzter, 1993). Recent above-ground studies with membrane-fed H_2 demonstrated that this approach was effective for denitrification (Lee and Rittman, 1999). The technology proposed here for *in situ* autotrophic denitrification addresses the safety concerns of water utilities and enables H_2 to be delivered to the subsurface at known concentrations in a very precise and controlled manner.

Methods, Procedures, and Facilities

General Procedure

Laboratory studies will be conducted in a model aquifer mesocosm. The model aquifer mesocosm will consist of a plexiglass tank measuring 1 m high by 20 cm wide and 3.0 m long and filled with aquifer material. This aquifer material will be representative of a nitrate contaminated site in Minnesota and the conditions employed in the experimental design also will be representative of the selected site. Approximately 10 cm from one end of the microcosm, a series of membranes will be installed across the width of the tank to deliver H_2 to the model aquifer. The membranes will be installed within a screened enclosure, thus approximating the conditions of delivery in conventional well installation. Because of the configuration of the tank and the membrane spacing across the width of

the tank, the data interpretation will be reduced to a one-dimensional analysis of the process without the complexity of down gradient dispersion. Sampling ports will be installed in the aquifer down gradient of the H_2 injection point. The sampling ports will be spaced closer together (10 cm) close to the injection point, and farther apart (25 cm) as one moves down-gradient from injection point. Water samples drawn from the sampling points will be analyzed to characterize gas transfer and denitrification kinetics.

A synthetic groundwater will be pumped through the model aquifer from a reservoir via an FMI metering pump. The groundwater flow-rate will be set to match the highest groundwater velocity anticipated at the selected nitrate-contaminated site. The composition of the groundwater will be representative of the composition of the water at the selected site (pH, nitrate concentration, alkalinity, TOC, etc.). The study will be conducted in a temperature-controlled room set at the approximate groundwater temperature (10°C). To ensure a good distribution of the groundwater flow in the model aquifer, the mesocosm will be equipped with a flow distributor at the tank inlet, consisting of a perforated baffle drilled with 1.5 mm holes across the depth and width.

A hollow fiber membrane supplied by Celgard (Charlotte, SC) will be used to supply H_2. A stitched fabric of hollow fiber membranes will be installed to ensure that H_2 is uniformly delivered. The membranes are made of microporous polyolefins and have been used in natural water environments in long term studies without observed losses in performance (Semmens and Gantzer, 1993). These membranes are highly gas permeable; therefore, the rate of gas transfer is dependent on the rate of gas diffusion into the surrounding groundwater.

Analytical Methods

Water samples will be collected from the sample ports periodically in order to quantify H_2 dissolution and consumption. In addition, changes in nitrate and nitrite concentrations will be monitored. Dissolved oxygen, alkalinity, pH, conductivity, total organic carbon (TOC) and heterotrophic plate counts (HPC) also will be analyzed to assess the impact of H_2 addition on the water quality. All analyses will be conducted according to Standard Methods, using EPA-approved methods.

Dissolved H_2 will be monitored using headspace analyses and gas chromatography. In addition, a H_2 detector developed by the Minnesota Pollution Control Agency (MPCA) will be used in parallel testing to verify its performance and to determine if it can be used in field scale monitoring. Nitrates and nitrites will be monitored with ion selective electrodes.

The introduction of H_2 will foster biological activity in the groundwater and the growth of microorganisms in the aquifer, particularly around the point of injection, and therefore may cause a decline in hydraulic permeability. To evaluate the potential impact of accumulating biomass the mesocosm will be equipped with manometer ports to assess any changes in head across the biologically active zone. In addition, occasional cores of aquifer material will be removed from the mesocosm to measure the local concentrations

of biomass. With these measurements, the growth of biomass and its migration downgradient will be assessed in a preliminary manner.

Modeling

The kinetics of denitrification will be modeled using sequential Monod kinetics. The mesocosm will be modeled as a plug flow reactor, verified via a tracer study using bromide. The resulting data will be employed to calculate the reactor dispersion number and to correct for dispersion, if any, in the denitrification data.

Related Research

Current research by the principal investigators concerns the use of membrane-fed H_2 for the support of biological anaerobic dehalogenation of perchloroethene and trichloroethene. This research focuses on membrane gas transfer behavior under groundwater conditions and on the use of H_2 by indigenous microorganisms. Dr. Semmens has an additional funded project to investigate the use of membranes to support nitrification and denitrification for wastewater applications.

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